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Vol. XXIII. No. 3 MAY 1950 Price 1s. Annual subscription 6s. ($1·30 in Canada and U.S.A.)

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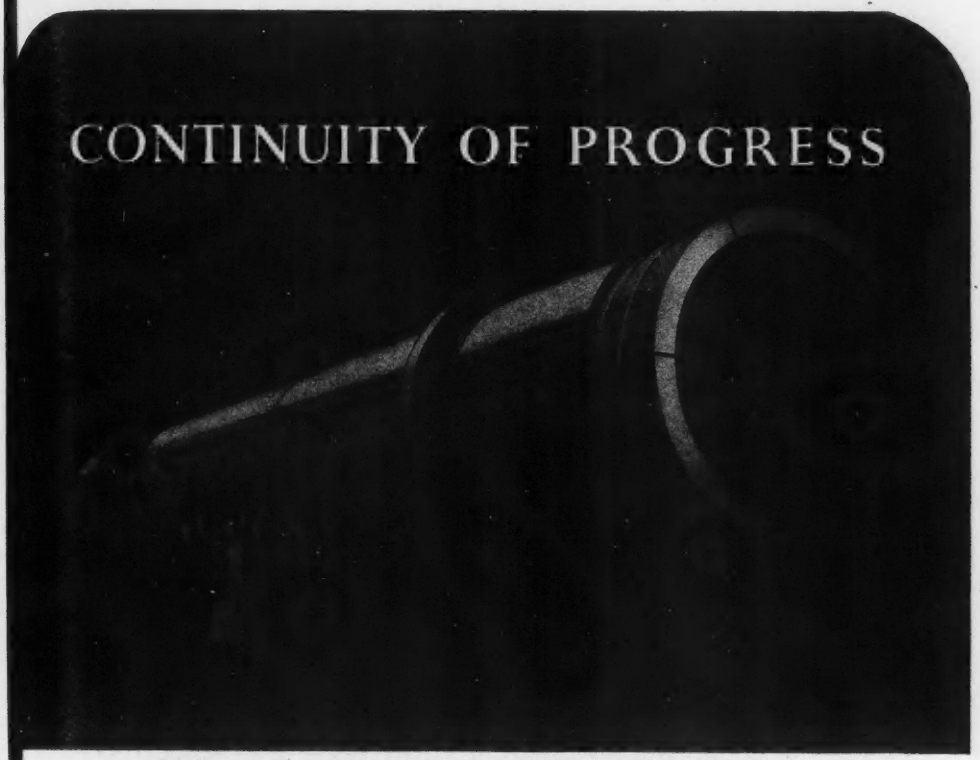

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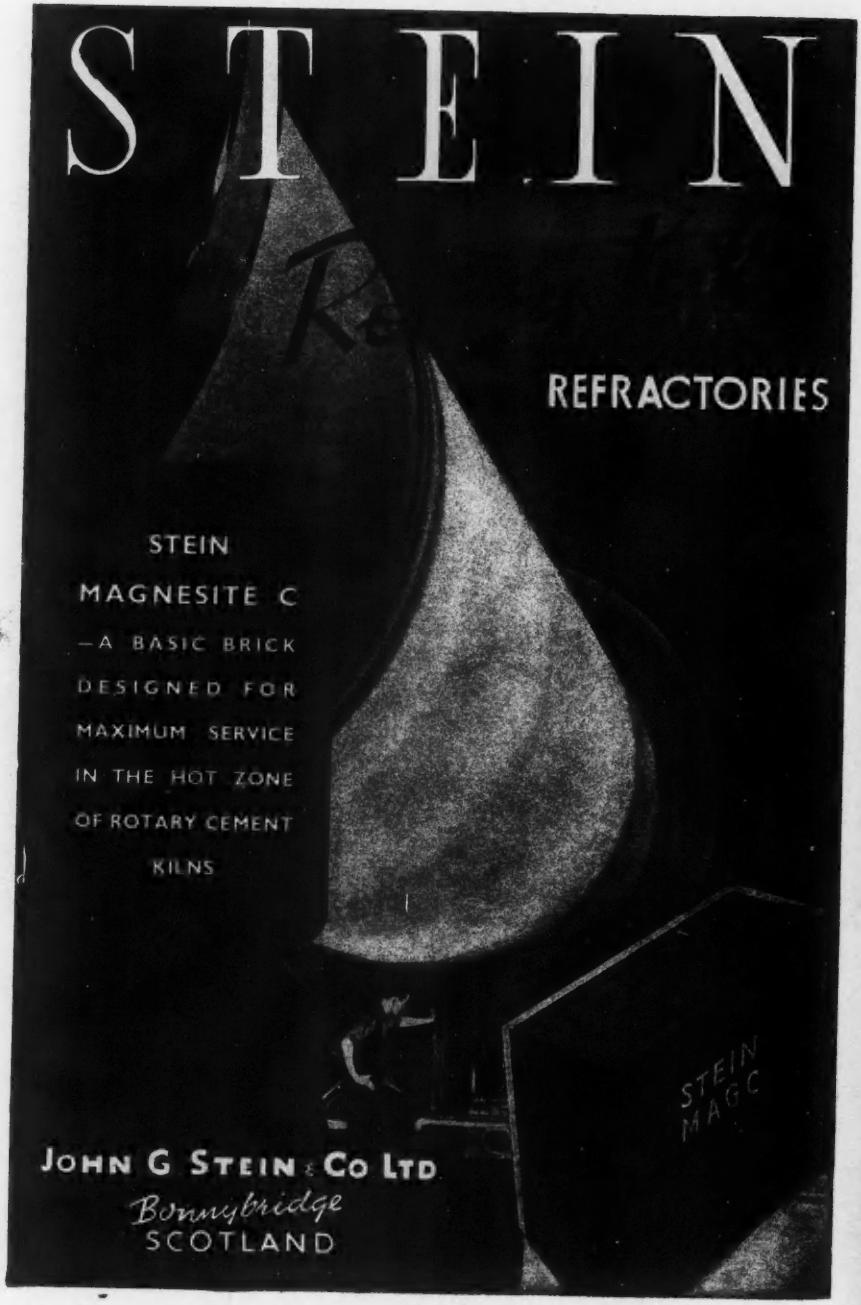
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PUBLISHED BY
CONCRETE PUBLICATIONS LIMITED
14 DARTMOUTH STREET, LONDON, S.W.1
TELEPHONE: WHITEHALL 4581.
TELEGRAPHIC ADDRESS: CONCRETIUS, PARL. LONDON

PUBLISHERS OF
"CONCRETE & CONSTRUCTIONAL ENGINEERING"
"CONCRETE BUILDING & CONCRETE PRODUCTS"
"CEMENT & LIME MANUFACTURE"
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VOLUME XXIII. NUMBER 3 MAY, 1950

Examination of the Hardening of Portland Cement by an Electronic Microscope.

IN an article in "Travaux," (January, 1950), M. D. Boutet discusses from various points of view the nature and properties of concrete, and in particular Portland cement concrete. He expresses the view that cement concrete should not be considered as a mixture of two phases, one continuous and inherently cohesive (the cement matrix) and the other discontinuous and composed of grains of inert stones embedded in the matrix. The particles of cement are transformed upon hydration into needles and clusters of crystals which appear to have reciprocated affinity at certain of their points. The author considers that, because of a similar affinity, the crystals likewise adhere to the sides of the pieces of aggregate. This affinity exists because the aggregate contains one or more constituents comparable with those of the cement, notably silica, lime, and alumina. It is because of the affinity, measured by the adhesion between the cement and aggregate, that the best Portland cement concretes have aggregates in which silica or calcium predominates. In support of his theory the author gives numerous photographs of Portland, high-alumina, expansive, and other cements in various stages of setting and hardening.

The photographs were taken by an electronic microscope in the laboratory of the Ponts et Chaussées of France. The microscope gives a magnification of 5,000 times on a fluorescent screen, and photographs of the image can be enlarged to give a total magnification of 100,000 times. The photographs reproduced in the following relate to Portland cement only and the linear enlargement is 5,000, that is the side of each illustration represents an actual length of about 10 microns. The size of the particles of cement shown is between 1 and 10 microns.

Before hydration and crystallisation of the hydrated constituents, the grains of cement appear to assemble in chains. *Fig.* 1 shows Portland cement fifteen minutes after mixing with water. The particles which are grouped in chains are very

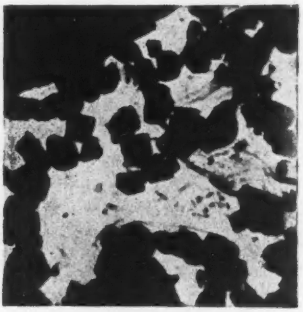

Fig. 1.—Portland Cement : 15 Minutes.

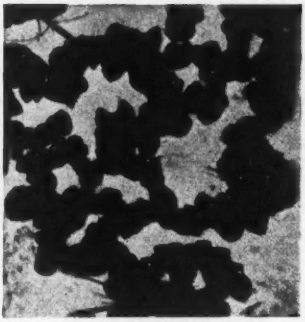

Fig. 2.—Portland Cement : 1 Hour.

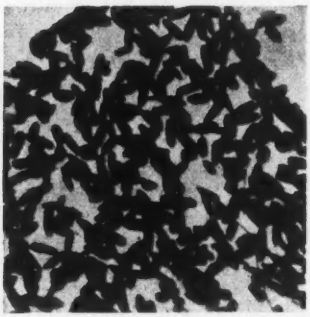

Fig. 3.—Portland Cement : 30 Minutes.

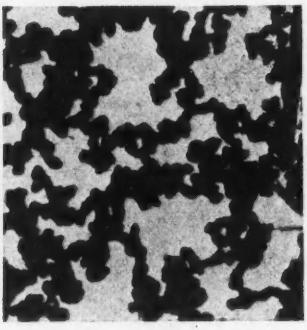

Fig. 4.—Portland Cement : 65 Days.

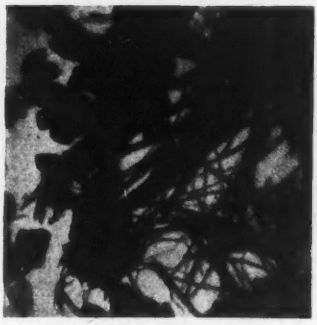

Fig. 5.—Portland Cement : 30 Minutes.

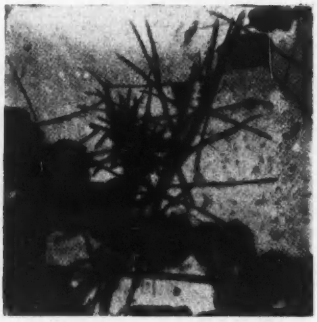

Fig. 6.—Portland Cement : 1 Hour.

fine, being less than 1 micron. Hydration has hardly commenced. The chains are joined to the largest particles and adhere to them as they would to inert particles of aggregate. *Fig.* 2 shows the same Portland cement one hour after mixing and shows the grouping of particles, such as the dicalcium silicate, that set slowly. *Figs.* 3 and 4 show chains of much finer grains, which after 65 days (*Fig.* 4) show a tendency to regroup differently. The clusters of micro-crystals form into chains, but the particles remain firmly connected at their points of contact.

Figs. 5 and 6 give an indication of the setting of Portland cement 30 minutes and one hour after mixing. There appear, between the particles of about 1 micron in size, fine needles which are entangled one with another, and the ends of which are attached to the sides of particles of greater size in the same manner as they would be attached to pieces of aggregate. The photographs support the theory that there are two very different constituents in Portland cement, namely, tricalcium

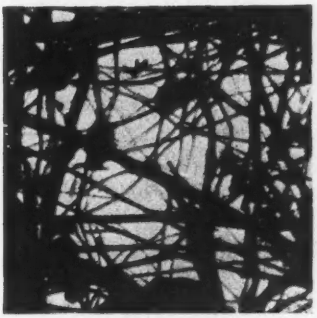

Fig. 7.—Portland Cement: 1 Day.

Fig. 8.—Portland Cement: 90 Days.

silicate, which is the constituent promoting initial hardening, and dicalcium silicate, which promotes the subsequent slow increase of hardening. All the photographs reproduced here are of the same Portland Cement, the differences being due to the smallness of the sample and the dispersion of the crystals.

The progressive crystallization results in the formation of more needle-like crystals in the heart of the continuous phase and, as seen in *Figs.* 7 and 8, become more closely interwoven. The denseness of the resulting mesh is a characteristic of the dilution of the cement. A few grammes of cement in a litre of water, as in some microscopic examinations, give a solution that is about a thousand times more diluted than cement mortars containing the minimum amount of water.

The crystals of the aluminates are generally hexagonal lamini, needle-like, or spherical. The spherical crystals appear generally in Portland cement, in the hydration of which the first crystals, in the form of thick needles, are probably of gypsum. The lime in Portland cement seems to produce needle-like or spherical crystals.

The Developments of Magnesian Cements.

THE most common form of magnesian cement is magnesium-oxychloride or Sorel cement (Sorel investigated the material in 1868), the base of which is magnesite ($MgCO_3$) calcined at not more than 1,000 deg. C. When mixed with a 20 per cent. solution of magnesium chloride, magnesium oxychloride (according to Lukens, quoted by Lea and Desch, $3\ MgO.MgCl_2,11H_2O$) is formed, and this compound, when mixed with an inert filler, is used as a floor covering. It is subject to attack by water, and corrodes iron. The composition of magnesian-chloride cement was discussed in our number for January, 1950, page 19.

British Standard Specification.

In accordance with British Standard No. 776, 1938, the composition (by weight) of the calcined magnesite must be: MgO, not less than 87 per cent.; CaO, not more than 2·5 per cent.; CO_2, not more than 2·5 per cent.; loss on ignition, not more than 8 per cent.; the sum ($MgO+CaO+CO_2+$loss on ignition) must be not less than 99·5 per cent. The composition (by weight) of magnesium chloride must conform to the following: Magnesium compounds expressed as Mg, not less than 11·25 per cent.; chlorides expressed as Cl, not less than 34·5 per cent.; calcium compounds expressed as $CaCl_2$, not more than 1 per cent.; sodium and potassium compounds ($NaCl+KCl$), not more than 2 per cent.; and sulphates expressed as $MgSO_4$, not more than 0·5 per cent.

Magnesian Cement for Concrete.

The use of magnesian cement for making concrete is considered by Sr. M. Steffen in "Cemento-Hormigon" for May, 1948. In spite of the high early compressive strength of this cement compared with Portland cement, it has not yet been possible to make a magnesian cement suitable for concrete. In the writer's opinion it would be necessary for the manufacture to be similar to that of Portland cement, that is rigorous control of the proportioning of the raw materials, calcination in a rotary kiln, and fine grinding. There remains the determination of the most suitable amount of active MgO in a magnesian cement of high strength. The problem of obtaining a magnesian cement suitable for concrete construction generally is far from solved, although it is used in structures in potash mines owing to its greater resistance to attack by the chemicals encountered.

The production of a good magnesian cement is stated to require magnesite of regular composition having not less than 80 per cent. of MgO and not more than 2 per cent. of CaO. The calcination of the magnesite must be made at a uniform temperature not exceeding 1,000 deg. C. Calcination in a muffle-furnace or a vertical kiln for a long time at 750 deg. C. has proved effective. In a rotary kiln the product passes too quickly through the calcining zone and the temperature must therefore be much higher. The permissible temperature

depends on the CaO content. If a magnesite contains no CaO a temperature of 1,000 deg. C. can be applied and the loss on ignition of the product may be less than 3 per cent., but if, for example, a magnesite contains 4 per cent. of CaO it must be calcined at a temperature below 900 deg. C. A result of calcination at a low temperature is an increase in the loss on ignition, and the German standards limit this loss to 9 per cent. A magnesite calcined at a high temperature contains a greater amount of active magnesia and results in compressive strengths higher than are attained by a magnesite which has a large loss on ignition, assuming that the $CaCO_3$ remains as an inert material not reacting with the chloride. Thus, for making concrete the proportion of aggregates must be lower than for a magnesite calcined at a higher temperature and free from lime.

In the manufacture of magnesian cement the lime plays the same part as does the magnesium in Portland cement; that is, the amount of lime must not exceed 5 per cent., which is the limiting amount of magnesia in Portland cement of good quality.

It is important to determine the most suitable proportion of MgO in a magnesite for the manufacture of magnesian cement. The German regulations specify a minimum of 75 per cent. in the calcined magnesite. Concrete made with a magnesite low in MgO must have less aggregate than when the MgO content is high, but it has been shown that pure MgO does not give the strengths that are obtained with a magnesite containing 75 per cent. of MgO. A suitable amount of MgO seems to be between 75 per cent. and 92 per cent., the actual amount to give the greatest strength being determined by tests in each case.

For flooring compositions it is generally recommended that the chloride solution should not exceed 23 deg. Baumé, but for magnesian-cement concrete the solution should be between 28 deg. and 31 deg., as there must be sufficient solution to react with the silicates and oxides in the magnesite and also with the silica in the aggregates. The magnesian silicates so formed render the concrete less sensible to humidity. A mixture of 4 parts (by volume) of calcined magnesite and 8 parts of quartz and sand with a magnesian-chloride solution of 29 degrees Baumé gave a concrete that after 48 hours had a compressive strength of 7,467 lb. per square inch. A mixture of equal parts of magnesite and aggregate and a solution of 31 degrees Baumé had a compressive strength after 48 hours of 10,297 lb. per square inch and a tensile strength of 1,266 lb. per square inch.

Although magnesian-cement concrete has a much higher strength at an early age than Portland-cement concrete there is little or no increase in strength with age, as has been shown by tests at six months, and in some cases there is a decrease in strength. Tests made by Dr. Zollinger at Karlsruhe show that the compressive strengths of specimens made with neat magnesian-cement paste made from magnesite calcined at 1,000 deg. C. are 8,960 lb. per square inch at 24 hours, 11,066 lb. per square inch at three days, 11,251 lb. per square inch at 7 days, and 11,777 lb. per square inch at 28 days. Of importance to the engineer, however, are the strengths of concrete at, say, five or ten years; much research is yet required, and some is now proceeding

Magnesian Cement Calcined at High Temperature.

The notes in the foregoing deal with caustic magnesian compounds, but a German patent describes the manufacture of a magnesian cement calcined at 1,500 deg. C. which resists water as well as does Portland cement, but instead of a magnesium-chloride solution an anhydrous magnesium salt is used. An advantage of this cement is that it contains no ferrous oxide and that steel in concrete made therefrom is not attacked. Generally magnesite calcined at a temperature exceeding 1,100 deg. or 1,200 deg. C. does not react with hydrated chloride, but by using magnesite calcined at a high temperature with anhydrous magnesium chloride, added in the form of a powder, a magnesian cement is obtained that gives to the inert magnesite a powerful catalyser as the powder dissolves in the mixing water forming hydroxide of magnesia.

A Stable Magnesian Cement.

A stable magnesian cement said to have good mechanical properties has been developed by M. A. M. Fleuret, and is described in a recent number of "Chimie et Industrie." The cement sets only after several hours, and it is recommended that it should not be removed from the moulds until at least seven hours after mixing. The full strength is developed in about 28 days and some representative strengths of mixtures of the cement and bauxite or silica, or both, are: Compressive strength, 27,000 lb. per square inch; tensile strength, 2,060 lb. per square inch; modulus of rupture, 4,267 lb. per square inch. The greatest strengths are obtained when the mixture is ground to a fineness such that there is no residue on a 900-mesh sieve. Hardened specimens had no appreciable defects after being subjected to a jet of water for 100 hours, immersion in boiling water for one hour, and rapid heating and cooling alternately for 40 hours.

According to a description in "Building Science Abstracts," the cement consists of natural magnesia obtained from natural calcium-free magnesium carbonate burned at 900 deg. C., anhydrous thorium sulphate, and magnesium chloride of density 1·27 to 1·29 deg. Baumé. The composition of the finely powdered mixture is: MgO, 37 per cent.; $Th(SO_4)_2$, 7 per cent.; and $MgCl_2$ solution, 56 per cent.

Export of British Cement.

THE Ministry of Works reports that the value of cement (including Portland cement, high-alumina cement, gypseous, and other building cements) exported from Great Britain in the year 1949 was £8,668,494. This compares with £1,284,576 in 1938, £4,263,592 in 1946, £3,666,657 in 1947, and £7,300,030 in 1948.

Nomogram for the Compound Composition of Hydrated Limes.

Two nomograms for obtaining rapidly the compound composition of hydrated limes from the oxide analysis are given by Mr. E. M. Levin in the Bulletin of the American Society for Testing Materials, December, 1949. A general nomogram (*Fig.* 1) can be applied to any commercial hydrated lime and gives values accurate to within 0·5 per cent. A special nomogram (not reproduced) is applicable only to some dolomitic limes. The significance of the unhydrated-oxide content is stressed.

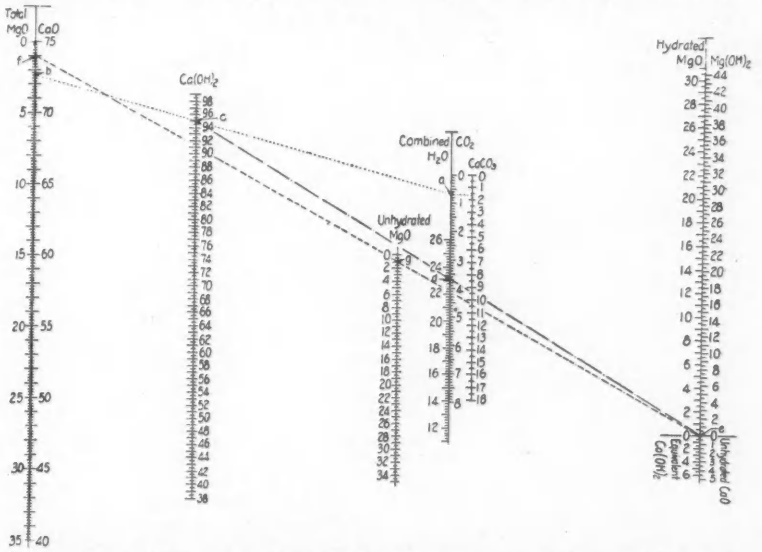

Fig. 1.—General Nomogram for obtaining the Compound Composition of any Commercial Hydrated Lime from the Oxide Analysis.

In some notes accompanying the nomograms Mr. Levin states that hydrated limes can be classified in three major groups on the basis of the total magnesia content, namely, (1) High-calcium limes containing less than 5 per cent. total magnesia ; (2) Dolomitic limes containing more than 25 per cent. magnesia ; (3) Magnesian limes containing between 5 and 25 per cent. magnesia. An American specification for hydrated lime requires the total free (unhydrated) calcium oxide (CaO) and magnesium oxide (MgO) in the hydrated product not to exceed 8 per cent. by weight calculated on the " as-received " basis. Determination of the unhydrated-oxide content of a lime is of obvious importance because of this limit. Investigations at the National Bureau of Standards have established a method of calculating the compound composition, including the unhydrated oxide content, from the chemical analysis. The chemical analysis includes determinations for " free " H_2O, combined H_2O, CO_2, SiO_2, R_2O_3, CaO, and MgO.

The method of calculating the compound composition is based essentially on the premise that CaO hydrates completely before MgO and then carbonates before MgO. In the calculations, CO_2 (usually less than 2 per cent.) is allotted to an equivalent amount of CaO to obtain the amount of $CaCO_3$ present. The remaining CaO is allotted to an equivalent amount of combined H_2O to obtain the amount of $Ca(OH)_2$ present. The remaining combined H_2O is allotted to an equivalent amount of MgO to obtain the amount of $Mg(OH)_2$ present. Finally, the remaining MgO represents the unhydrated-oxide content. If the amount of combined H_2O is insufficient to account for all the available CaO, some of the CaO is also unhydrated. In this event the combined H_2O is allotted to an equivalent amount of CaO to obtain the amount of $Ca(OH)_2$ present. The remaining CaO exclusive of that which is carbonated is unhydrated, and this amount is added to the MgO to obtain the total unhydrated oxides. The SiO_2 and R_2O_3 are considered to be uncombined, but only a small percentage of these oxides is usually present.

In the following derivation of the percentage of unhydrated oxide, the formula for the oxide represents the percentage of that component present. The derivation applies only to the common case in which all of the CaO is hydrated.

CaO equivalent to CO_2, $1{\cdot}275\ CO_2$.

CaO remaining, $CaO - 1{\cdot}275\ CO_2$.

Combined H_2O equivalent to CaO remaining, $0{\cdot}3213\ (CaO - 1{\cdot}275\ CO_2)$.

Combined H_2O remaining, combined $H_2O - 0{\cdot}3213\ (CaO - 1{\cdot}275\ CO_2)$.

Hydrated MgO, $2{\cdot}238$ [combined $H_2O - 0{\cdot}3213\ (CaO - 1{\cdot}275\ CO_2)$].

Unhydrated MgO (per cent.), total MgO $- 2{\cdot}238$ [combined $H_2O - 0{\cdot}3213$ $(CaO - 1{\cdot}275\ CO_2)$].

Having determined the percentage of unhydrated oxide, the compound composition is obtained simply by addition or subtraction, as follows :

$CaCO_3 = CO_2 +$ (CaO equivalent to CO_2).

$Ca(OH)_2 =$ (CaO remaining) + (combined H_2O equivalent to CaO remaining).

$Mg(OH)_2 =$ (combined H_2O remaining) + (hydrated MgO).

Unhydrated MgO = (total MgO) − (hydrated MgO).

Example.

Fig. 1 also illustrates the method of using the nomogram for a high-calcium lime having the following oxide analysis (in percentages) : CO_2, 0·70 ; CaO, 72·60; Combined H_2O, 23·06 ; Total MgO, 1·04 ; " Free " H_2O, 0·53 ; SiO_2, 0·74 ; R_2O_3, 0·60.

The procedure is as follows :

Draw line ab (CO_2 to CaO).

At right of point a read $CaCO_3 = 1{\cdot}6$ per cent.

At point c read $Ca(OH)_2 = 95{\cdot}0$ per cent.

Draw line cd [$Ca(OH)_2$ to combined H_2O] and extend to point e (hydrated MgO).

At point e read $Mg(OH)_2$ = nil.

Draw line ef [$Mg(OH)_2$ to total MgO]. At point g read unhydrated MgO = 1·0 per cent.

Surface Area of Hydrated Portland Cement.

RESEARCH on the adsorption of nitrogen, oxygen and argon of hydrated Portland cement is described in a paper, entitled "Surface Available to Nitrogen in Hydrated Portland Cement," by Mr. Raymond Q. Blaine and Mr. Harold J. Valis, published as Research Paper No. 1967 of The National Bureau of Standards of the United States Department of Commerce.

In an introduction to the paper it is stated that the low-temperature adsorption test, in which nitrogen or another inert gas is adsorbed at or near the boiling point of the gas, has been used for a number of years as a measure of the surface areas of particulate materials. It is also used to measure the internal surface of porous materials, that is the surface of pores large enough for the gas molecule to enter. Hydrated Portland cement paste is a porous solid, as evidenced by water permeability and water absorption measurements. However, different cements and different quantities of mixing water used in making the neat paste, as well as different curing conditions, result in different pore structures in the hydrated specimens. Furthermore, there is evidence that changes take place in the pore structure and crystal form as cement continues to hydrate. Powers and Brownyard[1] made studies of the internal surface areas of hydrated Portland cement pastes by using water vapour as the adsorbate. In the present study it seemed desirable to use a gas that would be less reactive with the cement constituents in order to measure the internal surface areas of the partially-hydrated Portland cement pastes. The purpose of this study was to determine some of the variables of the nitrogen adsorption method, the applicability of the low-temperature adsorption method to the study of hydrated cements, and the precision of the test method. It was also desired to determine the effect of various factors such as storage, age and water-cement ratio of hydrated paste on the surface areas available to nitrogen.

Methods of Test.

Cement pastes were made by using water-cement ratios of 0·25, 0·40 and 0·55 by weight. The cement and water were mixed in a beaker for 5 minutes by means of a spatula. The paste was then poured into paraffin-lined brass moulds ½ in. in diameter and 2 in. deep. The mould was sealed to a brass plate with resin-paraffin mixture previous to filling with the paste. The mould with paste was stored in moist air for the first 24 hours. For storage at 21 deg. C. the 90 per cent. relative humidity moist cabinet ordinarily used in cement testing was used. For storage at 5 deg. C. the mould containing the specimens was stored in a tight jar containing a small quantity of distilled water, which was immersed in a constant-temperature bath maintained at 5 deg. C. A similar procedure was used for storage at 38 deg. C., except that the jar with mould was placed in an oven maintained at 38 deg. C. After 24 hours the specimens were removed from the moulds, stripped of any adhering paraffin, and stored at 5, 21, or 38 deg. C. over distilled water in closed

containers or in water in the regular cement-specimen storage tank maintained at 21 deg. C.

Twenty-four hours after casting, some specimens were broken to granules in a mortar. These granules were sieved, the 10 to 20-mesh material being saved for some specimens. For others, the 20 to 50-mesh or the 50 to 100-mesh material was saved for test. Additional specimens were broken into granules and sieved after various periods of storage immediately before test.

Specimens were sealed into sample holders at 1, 3, 7, 28, and 84 days after casting. The samples were immediately evacuated, and the adsorption tests were made the following day. The coating formed on water-stored specimens was scraped off before test.

A piece of closed-off glass tubing was placed between the specimen and the top seal to prevent drying of the cement specimen in the sealing operation. The sample was then evacuated to less than 1 mm. Hg at room temperature for about six hours by means of a mechanical vacuum pump. The specimen holder was then attached to the adsorption apparatus and evacuated by means of a mercury diffusion pump for about 16 hours. The vacuum attained in the system was about 1×10^{-6} mm. of mercury as measured by means of a McLeod gauge. An oven was placed around the sample container after attaching it to the apparatus for the tests in which the sample was evacuated at 100 deg. C. to 110 deg. C. or 200 deg. C. to 210 deg. C.

Specimens were weighed before sealing into the sample containers. In order to determine the loss of water, the sealed specimen holder with the sample was weighed before evacuation and again immediately after the adsorption test. The original weight of the sample minus the loss during evacuation was taken as the basis for computing the surface area per gramme and also for computing the loss of water in evacuation. Ordinarily the specimen tested had a dry weight of 7 gr. to 10 gr. depending, in part at least, on the water-cement ratio in the original paste.

The apparatus used for determining the adsorption isotherm was of the volumetric type, which has previously been described[2]. The volume of the sample bulb not occupied by the solid portion of the sample was determined by means of helium, which had been passed over activated charcoal in a liquid nitrogen bath just before admission to the adsorption apparatus. The volume of helium admitted was determined from four pressure-volume measurements. Four additional pressure-volume measurements were made with the helium to determine the volume of the sample bulb not occupied by the solid. This calibration was made with the sample bulb immersed in liquid nitrogen or oxygen, depending on the gas to be adsorbed. After the helium calibration the sample was evacuated for two hours at room temperature.

Water-pumped tank nitrogen, purified by passage over magnesium perchlorate, chabasite, copper turnings at 400 deg. C., and then through magnesium perchlorate immediately before admission to the apparatus, was used for the adsorption measurements with most samples. The nitrogen entering the adsorption apparatus

was allowed to come to room temperature and its volume determined, after which the nitrogen was admitted to the sample bulb. After equilibrium had been attained (usually in about 20 minutes but at times longer than 1 hour), the volume of nitrogen not adsorbed was determined. Additional nitrogen was then added either from the burette system or from the tank, and the process was repeated. All volumes were calculated on the basis of the volume at 0 deg. C. and 760 mm. mercury pressure. Corrections were made for density of the mercury in the manometers, the changes in scales with temperature, and for the "nonideal" behaviour of the gas in the dead space around the sample. Five or more values at partial pressures between 0·05 and 0·35 on the adsorption isotherm were determined for each of the samples. Additional values were obtained up to partial pressures of 0·5 to 0·7 on most of the samples, and on one sample the adsorption curve was obtained to above 0·9 partial pressure, after which desorption values were obtained.

The vapour pressure of the adsorbate was determined from the condensed adsorbate in a vapour pressure bulb in the bath alongside the sample, and the glass tube leading from the bulb to the manometer was jacketed with a larger tube in order to measure the vapour pressure near the adsorption bulb rather than at the surface of the bath, which may be slightly cooler than the sample. Oxygen gas was used as the adsorbate on one sample, using a liquid-oxygen bath. Argon was used as the adsorbate on one sample using a liquid-oxygen bath and on another sample using a liquid-nitrogen bath.

Surfaces areas of all samples were evaluated by means of the BET equation[3] as follows:

$$\frac{P}{V(P_0-P)} = \frac{1}{V_m C} + \frac{(C-1)\,P}{V_m C\,P_0}$$

where P is the pressure of the adsorbate, P_0 the vapour pressure of the adsorbate at temperature of bath, V the volume of gas adsorbed (standard temperature and pressure) at pressure P, V_m the volume of gas required for the monolayer, C the ke exponential $(E_1-E_L)/RT$, k is a constant, E_1 the heat of adsorption, E_L the heat of liquefaction, R the gas constant and T is absolute temperature.

$P/V(P_0-P)$ was plotted against the partial pressure P/P_0. The slope and intercept of a line drawn through the points on the graph between partial pressures of 0·05 and 0·30 were used to evaluate V_m and C. The area on the surface occupied by each molecule corresponds with those calculated by Emmett[2] from the liquid or solid density, molecular weight, and Avogadro's number. The values for the area occupied by each molecule as used for the surface area calculations were as follows: N_2, 16·2 sq. A; O_2, 14·1 sq. A; argon at liquid-nitrogen temperature, 12·8 sq. A and at liquid-oxygen temperature, 14·4 sq. A.

In order to study the pore diameters of the hydrated specimens, isotherms were calculated on the basis of the values of V_m and C obtained for the particular samples[3]. Various values of n were substituted in the following equation and these calculated isotherms were superimposed on the adsorption isotherm.

$$V = \frac{V_m C x}{1 - x} \cdot \frac{1 - (n+1)x^n + nx^{(n+1)}}{1 + (c-1)x - cx^{(n+1)}}$$

where n is the maximum number of layers that can be adsorbed on the walls of the capillary, $x = P/P_0$, and, V, C, and V_m are the same as in the previous equation. The values reported are the results of single determinations. In order to determine the precision of the test results, five determinations were made in which the water-cement ratio, curing conditions, age, and temperature of evacuation were nominally constant. These five determinations were made on different days over a period of about three months during the period when most of the other tests were made.

Summary of Results.

Higher surface values were obtained on specimens evacuated at the higher temperatures. The hydrated cement ground to pass a No. 10 sieve and retained on a No. 20 sieve had higher surface values than did the whole specimens. The surface values of granulated specimens were lower for the smaller granules. The surface values obtained by use of nitrogen at liquid nitrogen temperature were about the same as those obtained with oxygen at liquid oxygen temperature, and argon at liquid oxygen or liquid nitrogen temperatures. The surface available to nitrogen was much less than that previously reported as available to water molecules. The surface values increased with age for specimens made with high water-cement ratio but not when made with a low water-cement ratio. The surface values of specimens stored in moist air at 38 deg. C. were higher than those of specimens stored at 21 deg. C. up to 28 days. The surface values of specimens stored in moist air at 5 deg. C. were approximately the same at one day as were those stored at 21 deg. C. or 38 deg. C., but increased more slowly with age than did those stored at the higher temperatures. The surface values of a Type I[4] cement were higher at 28 days and 84 days after storage in water than after storage in moist air. The surface values of pastes made of Type II and Type III cement were higher than those obtained with Type I cement neat paste at all ages of moist air storage. The surface values of Type II and Type III cements were about the same when stored in water as when stored in moist air, except at 84 days when the water-stored specimens had greater surface values. The pore diameter of the hydrated pastes was about 30 angstroms.

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[1] T. C. Powers and T. L. Brownyard. J. Am. Concr. Inst. **18**, 469 (1946).

[2] P. H. Emmett. Symposium on new methods for particle size determination in the subsieve range, Am. Soc. Testing Materials (1941).

[3] S. Brunauer. The absorption of gases and vapours, p. 153 (Princeton University Press, Princeton, N.J., 1945).

[4] Cement Type I, etc., refer to American standard cements which are described in this journal for May and July, 1949.

Research on Cement in Britain.

IN the following are given summaries of some recent reports of research by the Building Research Station on Portland and other cements.

Portland and High-alumina Cements.

It is stated in the "Report of the Building Research Board, 1948" (issued February 1950 by H.M.S.O. Price 1s. 6d) that studies on the silicate systems of interest in connection with the constitution of Portland and high-alumina cement and of blastfurnace slag have been resumed at the Building Research Station. It is stated that a necessary feature of the high-temperature work involved is the accurate control of the electric furnaces, and a new form of temperature controller has been installed. The limits of temperature attainable in practice by means of the platinum-rhodium alloy winding of the furnaces in general use is about 1,650 deg. C (3,000 deg. F); in an attempt to increase this range, a rhodium-wound furnace was constructed, but after a very short operation it failed. It is has therefore been necessary to investigate the possibility of using molybdenum or tungsten windings, in spite of their inconveniences, in an attempt to extend the work range to about 2,000 deg. C (3,600 deg. F).

Single crystals of some of the cement compounds have been prepared successfully in the laboratory. One of them, $3CaO.SiO_2$ has been the subject of X-ray studies at Birkbeck College under the direction of Professor J. D. Bernal. It emerges that there are three forms of $3CaO.SiO_2$—trigonal, monoclinic, and triclinic. The monoclinic form is the one found in Portland cement and the triclinic form is the one normally made in the pure state in the laboratory. This observation opens up a path for further investigations on the properties of cements. Single crystal X-ray studies of $2CaO.SiO_2$ are also in progress and the conditions of stability of the β, a, and a' forms of this mineral are being investigated.

Work carried out during the war gave new data on the constitution of high-alumina cement, and this is now being extended. The system is of greater complexity than Portland cement, and the problem of the compounds which are present, and their proportions, is some way from being solved. A step in the identification of the ferrites present has, however, been made by the use of micro-reflectivity measurements on polished sections under the microscope, while some new data on one of the aluminate constituents, "unstable $5CaO.3Al_2O_3$," have been obtained. These, together with evidence obtained by the use of a method of extraction successively by alkali and then acid, are beginning to throw more light on the constitution of this cement.

The system $CaO–SiO_2Al_2O_3–MgO$ is of interest in the study of Portland and high-alumina cements and of blastfurnace slag. Parts of it are accordingly being investigated in the laboratory, attention being paid in particular to the properties of glasses formed from quenched liquids in the relevant parts of the system.

Slags for Blastfurnace Portland Cement.

The possibility of increasing production of cement by making greater use of granulated blastfurnace slag was investigated by the Building Research Station during 1940-42, and an account of the experiments and the results obtained is now given in National Building Studies Technical Paper No. 3, " Investigations of Granulated Blastfurnace Slags for the Manufacture of Portland Blastfurnace Cement " (published by H.M.S.O. 1949. Price 9*d.*; by post 10*d.* 25 cents. in U.S.A.).

Samples of granulated slags from different works were prepared and ground, and tested with Portland cement clinker. The tests show that all the slags tested had hydraulic value which is not greatly affected by the method of granulation. The method of granulation, however, makes considerable difference to the density of the slag, the water retained after draining, and the ease of grinding. Most of the experimental cements satisfied British Standard No. 146 for Portland blastfurnace cement.

The following is an abstract of the summary in the document.

When the same cement clinker was used in a 65 : 35 mixture with the slags, and the mixtures were ground to the specified fineness, the results can be represented by

$$(C - 75) = 0{\cdot}38\ (m - 0{\cdot}72)G$$

where C is the strength at 90 days of 1 : 2 : 4 concrete, having a water-cement ratio of 0·60, expressed as a percentage of the strength of similar concrete made with undiluted Portland cement ; m is a modulus obtained from the chemical analysis of the slag and is equal to $\frac{CaO + MgO + \frac{1}{3}Al_2O_3}{SiO_2 + \frac{2}{3}Al_2O_3}$. The percentage of glass G is obtained by a microscopic test.

In general, hæmatite slags gave the best results, but there was considerable overlapping with basic and foundry-iron slags. The early strength was considerably affected by the ratio of gypsum to clinker and by impurities such as chlorides in the slag.

Altnough the existing knowledge concerning the glassy state in general, and the $CaO–Al_2O_3–SiO_2$ glasses in particular, is insufficient to permit detailed analyses, it appears likely that the upper limit of hydraulicity is reached when the glass becomes very unstable. At this upper limit the strength of a 65 : 35 blastfurnace Portland cement is not likely to exceed that of the parent Portland cement of the same fineness by a significant amount at ages up to 90 days.

The Analysis of Waste Gases.

THE use of oxygen analysers to maintain a continuous record of the waste gases from a cement kiln is described in " Rock Products " for August, 1949, by Mr. E. H. Gray, formerly research chemist of the Missouri Portland Cement Co., of St. Louis, Missouri, where three different types of oxygen-analysers have been installed on five kilns one of which is 311 ft. long by 11 ft. 3 in. by 10 ft. and four are 240 ft. long by 11 ft. 3 in. by 10 ft. The oxygen analysers were in use during part of the year 1947 and throughout the year 1948, and it is stated that as the burners became more familiar with the use of the apparatus and increased the time of oxidisation the coal consumption was less ; in the year 1947 the coal consumption was 136 lb. per barrel (360 lb.) of cement, in 1948, it was 130 lb. per barrel and in 1949 it was still less.

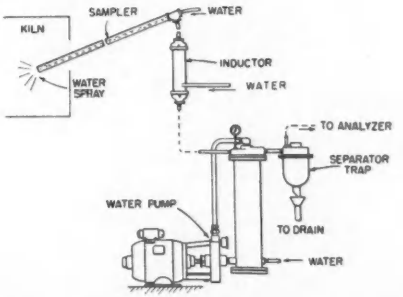

Fig 1.—Sampling System for Oxygen Analyser.

The kilns were normally operated with a deficiency of air and combustible material was present in the exit gases. A lower coal consumption resulted when a small amount of oxygen was maintained in the exit gases and the combustible material was then burned. It is said that oyxgen analysers can also be used to advantage on kilns which normally are fired with an excess of air. If too large an excess of air is carried, heat is lost as sensible heat of the gases. This loss can be reduced by lowering the excess air to the optimum value and maintaining this value with the aid of an oxygen analyser. Sensible heat losses are especially important in kilns with high exit-gas temperatures.

The most difficult problem in obtaining a continuous analysis is to obtain a sample of clean gas for the analyser, and it is important that all solid matter be removed from the gas flowing into it. The sampling system of the Bailey Meter Co. is shown in *Fig.* 1. The sample is delivered by means of a large water aspirator, the water for which is circulated by a centrifugal pump direct-connected to a $\frac{3}{4}$-h.p. motor. Make-up water, which is added to an inductor, also serves to cool the sample. A water spray at the end of the sample tube removes dust from the gas. A sampling system such as this has been in operation for over a year and

has required very little maintenance. The gas pump delivers about 1½ cu. ft. of gas per minute, a small part of which is required by the analyser and the rest is wasted. The use of such a large volume of gas results in a very quick response. A change in the coal feed will result in a complete change on the recorder in less than one minute. Two important precautions should be followed in installing this sample system. One is that the sample tube must be at an angle of 15 deg. or more from the horizontal and the other is that the water going to the sample tube spray should be filtered. Even with a water filter it has been necessary to clean the sample tube once a month. A pressure-switch has been installed to stop the pump motor when the pressure on the water flowing to the spray drops below a critical value.

Revision of British Standard for Low-Heat Portland Cement

THE requirements for the tests for strength, consistency of cement paste, setting time, and soundness in British Standard No. 1370 (1947) differ slightly from those in British Standard No. 12 (1947). Revisions recently made to B.S.1370 remove these differences. The standard sand used for cubes for the compressive test must now be such that not more than 10 per cent. by weight passes a No. 52 sieve. The quantity of water to produce a cement paste of standard consistency is equal to that required to give a paste in which the needle of a Vicat plunger settles to a point from 5 mm. to 7 mm. from the bottom of the mould. The cement paste used for the tests of setting time and soundness must be formed by gauging the cement with 0·85 of the quantity of water required for a paste of standard consistency. The initial setting time is determined when the needle does not pierce the block below a point about 5 mm. from the bottom of the mould.

Portland Cement and Plastics.

THE possibility of increasing the strength and reducing the shrinkage of Portland cement mortar and concrete by mixing plastic materials with the cement is described by Dr. R. A. J. Bosschart in " Cement " (Holland), Nos. 15, 16. Two groups of plastics are considered, those that remain hard at high temperatures and those that soften, and the chemical and colloidal-chemical effects are discussed.

A comprehensive expression for the compressive strength is $\frac{A}{b_m}\left(\frac{1}{W^2} + Bk\right)$, in which A and B are constants, W is the water-cement ratio, k is the percentage of plastic material, and b_m is the sum of the products of the proportion of particles of each size in the mixture and a factor which is 9 for sand, 220 for material passing a 40-mesh (per centimetre) sieve, and 350 for material passing an 80-mesh sieve.

The Cement Industry in Greece.

THE following is an abstract of a report on the Greek cement industry furnished by the British Embassy in Athens and issued by the Commercial Relations and Exports Department of the Board of Trade.

There are five cement companies in Greece with six factories and a total annual capacity of about 370,000 tons, as follows: General Cement Co. (Heraklis works, 100,000 tons; Olympus works, 50,000 tons); Titan Cement Co., (120,000 tons); Chalkis Artificial Portland Cement Co. (55,000 tons); Halyps Cement Co. (25,000 tons); Atlas Building Material Co. (20,000 tons). The present capital invested in the industry is estimated at about £1,500,000. In 1939 the industry employed about 1500 persons and its annual production was valued at about £600,000.

Total production in 1947 was 177,260 tons, and in 1948 288,176 tons; in 1939 it was about 335,000 tons. In 1949 production is expected to be about 310,000 tons. Since 1933, except for the war years, production has kept pace with consumption, small quantities of white cement only being imported; 22,728 tons were exported in 1948 to Near East markets. It is estimated that consumption may reach 550,000 tons by 1955.

Greek cement is all of the artificial Portland type. The four largest factories produce three qualities, namely, Greek type, containing up to 10 per cent. of Santorin earth added during the grinding of the clinker; "Strong," made from specially-burnt clinker without any addition (except gypsum); and "Very strong" for defence works and rapid hardening.

All the raw materials are available in Greece, including limestone, Santorin earth, Milos-island earth, marl from Aegina and Attica, iron pyrites residue, and gypsum from Crete. The fuels used for burning are coal and fuel oil and some local good-quality lignite; 95 per cent. of the fuels for burning have in the past been obtained from abroad. Oil consumption varies between 160 and 250 kg. per ton of cement. Imported coal has always been cheaper per calorie than local lignite. The development of lignite production foreseen in the Greek four-year recovery programme should, however, make possible the increased use of this fuel. The fuel used for drying is mainly imported oil or coal, some local lignite, and occasionally wood. Only the Olympus and Chalkis factories produce their own power; consumption per ton of cement is from 85 to 140 kwh.

Most of the machinery is imported, but equipment such as conveyors, dryers, wagons, scales, and feeding equipment can be made locally. In recent years some good quality castings and steel have been made in Greece from imported materials. About 50 per cent. of the present equipment is 25 years old and 17 per cent. at least 35 years old.

The 1948-49 recovery programme provides for new rotary kilns and other equipment to provide an additional capacity of 270,000 tons. After allowing for plant to be scrapped this should result in a net increased capacity of 84,000 tons in 1951. The four-year plan includes an expected additional net increase in capacity of 49,000 tons by 1953.

The plant at the Titan factory at Elcusis includes three Krupp kilns 10 ft. by 177 ft., 7 ft. 4 in. by 131 ft., and 6 ft. 6 in. by 131 ft., with daily capacities of 250 tons, 100 tons, and 50 tons respectively, and the raw material, clinker, and coal mills are also of Krupp manufacture. An expansion of capacity to 177,000 tons is planned. Equipment costing 959,000 dollars will be imported from Denmark, while 98,272 dollars will be spent in Britain and 10,400 dollars in Belgium.

The Heraklis factory at Drapetsona, Piraeus, has one Polysius kiln 8 ft. by 197 ft. and one Polysius kiln 9 ft. by 164 ft., with capacities of 380 tons and 140 tons a day respectively. The raw material and coal mills are by Polysius; one clinker mill is by Miag and the other by Polysius. Two kilns of 350 tons daily capacity and secondary equipment have been ordered in the U.S.A.

The Olympus factory at Volos (Ali Meria) has one 8 ft. by 131 ft. kiln and crushing plant supplied by Miag. The factory at Chalkis has one 8 ft. by 148 ft. kiln with a capacity of 170 tons a day and crushing and grinding plant by Miag. The Halyps works at Aspropyrgos-Scaramanga has one 6 ft. 6 in. by 135 ft. kiln with a capacity of 70 tons in 24 hours (the makers of the plant are not named). At the Atlas works at Myloi (Attica) there are a Humbolt kiln 6 ft. 6 in. by 115 ft., with a capacity of 70 tons per day and Humbolt crushers and grinders.

The chemical composition and physical properties of Greek cements are approximately as follows:—

	Cement with Santorin earth (per cent.)	Medium strong cement (per cent.)	Very strong cement (per cent.)
Insoluble residue	7 to 7½ (10% maximum)	½ (3 per cent. maximum)	—
Loss on ignition	1¾ to 2	1¾	¾
SiO_2	20	22	20
Al_2O_3	5	6	6
Fe_2O_3	2½ to 4	2½	4½
CaO	60	64	66
MgO	¾ to 1¾	1¾	1
SO_3	1	1½	1
Alkalis	⅞	½	—
	(hours)	(hours)	(hours)
Initial set	1½ to 2½	1½ to 2½	1½ to 2
Final set	5½ to 7½	4 to 6	5 to 6
Fineness (4,900 mesh)	12 (± 2)	7 (± 1)	4 (± 1)
Tensile strength	(lb. per sq. in.)	(lb. per sq. in.)	(lb. per sq. in.)
24 hours	—	242	213
3 days	284 to 327	427	427
7 days	370 to 427	484	498
28 days	455 to 540	569	519
28 days (Combined Storage)	683 to 640	711	597
Compressive strength			
24 hours	—	2134	3129
3 days	3698 to 3129	3840	6258
7 days	4978 to 4267	4978	7681
28 days	6258 to 4978	6401	8961
28 days (Combined Storage)	6969 to 6401	7112	9530
Specific gravity	2·9	3·05	3·1
Hydraulic modulus	2·03 to 2·18	2·10	2·14

Soundness is tested by the boiling and cold pat test.

Storage of Portland Cement in Paper Bags.

Experiments made by Rocla, Ltd., of Australia, on the effect of covered, but not air-conditioned, storage on the tensile strength of 1:3 cement mortar showed that there was a slow deterioration of cement when stored in paper bags. The rate of loss of strength was about 4 to 5 per cent. per month of storage.

Six 5-ply paper bags of cement were taken at random from a consignment. One bag was opened immediately and the contents tested. Then it was closed, wrapped in polyvinyl cloth, stored in its wrapping, and tested again after six months. The other five bags, which were not wrapped in polyvinyl cloth, were stored in a dry room and one was opened and tested every 28 days. The room was not air conditioned, and so conformed more or less to the fluctuations of humidity and temperature outside. The tensile strength was determined on mortar specimens, the mortar being composed of 3 parts of standard sand, 1 part of cement and 0·4 part of water.

The reduction of strength of the cement stored for six months wrapped in polyvinyl cloth was 5·5 per cent. after storage of the specimen in water for seven days, 12·5 per cent. after 28 days' water storage, and about 10 per cent. after 28 days' combined storage (1 day in damp air, 6 days in water, and 21 days in air). The strength of specimens made from the cement stored in unwrapped bags was reduced by 31·5 per cent. after seven days, 25·8 per cent. after 28 days' wet storage, and 23 per cent. after 28 days' combined storage.

In describing these tests (in the Journal of the American Concrete Institute for December, 1949), Rocla, Ltd., report being told that similar experiments, in which cement was stored in bags in a shed such as a contractor might use on a site, showed a loss of compressive strength of 28 per cent. after storage for six months, 40 per cent. after one year, and 54 per cent. after two years. The composition of the concrete specimens in this case was 1 : 5 by weight. It was also found that some of the loss of strength was recovered by storing the concrete specimens for some time. For example, when tested after 28 days, the compressive strength of concrete made with cement stored for six months in paper bags was reduced by 25 per cent., whereas when tested after six months the reduction was only 16 per cent.

A German Rapid-Hardening Cement.

A report on " Schmeltz " cement, which is exclusively made in Germany at the Hochofen Cement Works, Luebeck, is available at the German Division (Documents Unit) of the Board of Trade, 38 Cadogan Square, London, S.W.1. Microfilm copies will be supplied on request (the reference number of the document is F.D.2549/49). " Schmeltz " cement is so called because the materials are melted before being finely ground. Tests were first made of " Schmeltz " cement imported from Hungary in 1927. Until about the year 1930 the material was imported from Hungary and Belgium, and about this time production was started in Germany. The report gives the composition and properties of the material, and results of tests.

New Cement Works in El Salvador.

THE new cement plant under construction in El Salvador is expected to be in production at the end of the year 1950. The capacity will be between 34,000 and 40,000 tons a year. It is understood that import duties have been waived on the machinery and equipment, and that taxes will not be payable by the concern until the year 1965.

Cement Production in Argentina and Colombia.

THE production of Portland cement in Argentina in the year 1949 was 1,422,250 tons, compared with 1,250,000 tons in 1948 and 1,350,000 tons in 1947.

It is reported that 100,000 tons of Portland cement are being supplied from Chile to Argentina.

It is reported that the amount of cement produced in Colombia in the year 1949 was 475,777 tons, which is a record.

A New Book on Blastfurnace Slag.

A NEW book, in the German language, entitled "Hochofenschlacke," by F. Keil (published by Verlag Stahleisen M.B.H., Düsseldorf. Price 32.50 DM.), deals in great detail with the manufacture, properties, and uses of blastfurnace slag. Its use in the manufacture of cements is fully described.

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